

# Topological insulator in a Bi-Bi<sub>2</sub>Se<sub>3</sub> infinitely adaptive superlattice phase

T. Valla,<sup>1,\*</sup> Huiwen Ji,<sup>2</sup> L. M. Schoop,<sup>2</sup> A. P. Weber,<sup>3,4</sup> Z.-H. Pan,<sup>1</sup> J. T. Sadowski,<sup>5</sup> E. Vescovo,<sup>3</sup>  
A. V. Fedorov,<sup>6</sup> A. N. Caruso,<sup>4</sup> Q. D. Gibson,<sup>2</sup> L. Muehler,<sup>7</sup> C. Felser,<sup>7,8</sup> and R. J. Cava<sup>2,†</sup>

<sup>1</sup>*Condensed Matter Physics and Materials Science Department,  
Brookhaven National Lab, Upton, New York 11973, USA*

<sup>2</sup>*Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA*

<sup>3</sup>*National Synchrotron Light Source, Brookhaven National Lab, Upton, New York 11973*

<sup>4</sup>*Department of Physics, University of Missouri-Kansas City, Kansas City, Missouri 64110, USA*

<sup>5</sup>*Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA*

<sup>6</sup>*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

<sup>7</sup>*Institut für Anorganische und Analytische Chemie,  
Johannes Gutenberg-Universität, 55128 Mainz, Germany*

<sup>8</sup>*Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany.*

(Dated: August 15, 2012)

We report spin- and angle-resolved photoemission studies of a topological insulator from the infinitely adaptive series between elemental Bi and Bi<sub>2</sub>Se<sub>3</sub>. The compound, based on Bi<sub>4</sub>Se<sub>3</sub>, is a 1:1 natural superlattice of alternating Bi<sub>2</sub> layers and Bi<sub>2</sub>Se<sub>3</sub> layers; the inclusion of S allows the growth of large crystals, with the formula Bi<sub>4</sub>Se<sub>2.6</sub>S<sub>0.4</sub>. The crystals cleave along the interfaces between the Bi<sub>2</sub> and Bi<sub>2</sub>Se<sub>3</sub> layers, with the surfaces obtained having alternating Bi or Se termination. The resulting terraces, observed by photoemission electron microscopy, create avenues suitable for the study of one-dimensional topological physics. The electronic structure, determined by spin- and angle- resolved photoemission spectroscopy, shows the existence of a surface state that forms a large, hexagonally shaped Fermi surface around the  $\Gamma$  point of the surface Brillouin zone, with the spin structure indicating that this material is a topological insulator.

PACS numbers: 74.25.Kc, 71.18.+y, 74.10.+v

Three-dimensional (3D) topological insulators (TIs) have Dirac-like surface states in which the spin of the electron is locked perpendicular to its momentum in a chiral spin structure where electrons with opposite momenta have opposite spins [1–8]. The number of experimentally identified 3D TIs has grown since the initial discovery, now including the Bi<sub>1-x</sub>Sb<sub>x</sub> alloy [3], Bi<sub>2</sub>Se<sub>3</sub> and Bi<sub>2</sub>Te<sub>3</sub> and their mixed anion variants [6, 7, 9–11], GeBi<sub>2</sub>Te<sub>4</sub> and its PbSe-Bi<sub>2</sub>Se<sub>3</sub> variants [9, 12], TlBiSe<sub>2</sub> [13, 14], and SnTe [12]. Of these materials, Bi<sub>2</sub>Se<sub>3</sub> has been highlighted as a model system due to its large bulk gap and simple surface electronic structure - a single Dirac-like topological surface state (TSS) whose Dirac point resides inside the gap, essentially fully spin polarized and robust against the elastic scattering and scattering on phonons [4, 8, 15–19].

Bi<sub>2</sub>Se<sub>3</sub> is actually only one member of a family of compounds, called an “infinitely adaptive series”, between pure Bi metal and Bi<sub>2</sub>Se<sub>3</sub>, made by stacking integer numbers of bismuth bi-layers and Bi<sub>2</sub>Se<sub>3</sub> layers, in compounds of the type (Bi<sub>2</sub>)<sub>m</sub>(Bi<sub>2</sub>Se<sub>3</sub>)<sub>n</sub> [20]. Given the topological properties of the surface of Bi<sub>2</sub>Se<sub>3</sub>, and the fact that the bismuth bi-layer has been predicted to be a two-dimensional quantum spin Hall system [21], it is of interest to determine whether the superlattice material also has topological surface states. Thus far, however, these materials have been studied only structurally as small crystals, or in polycrystalline form [20]. Here we report the successful growth of large single crystals of the sim-

plest member of the infinitely adaptive series, i.e. Bi<sub>4</sub>Se<sub>3</sub> (m=n=1), stabilized for crystal growth by partial S substitution for Se, and present spin- and angle-resolved photoemission spectroscopy (SARPES) studies of its surface electronic structure. Our measurements reveal a hexagonally shaped surface state whose spin structure indicates that Bi<sub>4</sub>Se<sub>3</sub> is a new topological insulator. The compound is the natural bulk analog of recently described artificial material made by Bi adsorption on the surface of Bi<sub>2</sub>Te<sub>3</sub> [22]. Photoemission electron microscopy (PEEM) reveals that the material cleaves with mixed Bi-layer and Se-layer terminations of the exposed terraces. This prohibits the association of the TSS with either the Bi or Se terraces by (S)ARPES, but it shows that this material offers the unique opportunity for studying novel 1D topological physics near the terrace steps by nanometer-scale probes.

High purity elemental Bi (99.999%), Se (99.999%), and S (99.999%) were used for the Bi<sub>4</sub>Se<sub>2.6</sub>S<sub>0.4</sub> crystal growth, with a starting formula of Bi<sub>4.5</sub>Se<sub>2</sub>S; the excess bismuth was used as a flux and the S greatly enhances the selective crystal growth of the 4:3 phase. The pre-cleaned elements were sealed in clean quartz ampoules, heated to 850 °C for 1 day, and cooling over the period of 1 hour to 700 °C. The crystal growth involved cooling from 700 °C to 550 °C over a period of 25 h, followed by centrifuging. Single crystals up to 1 centimeter size were obtained, with high-luster cleavage faces. Single crystal X-ray diffraction data was collected on a

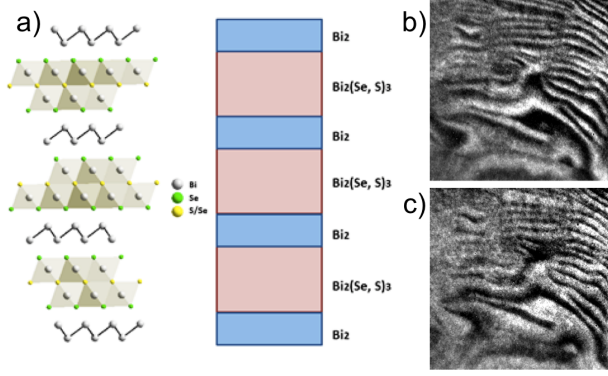


FIG. 1: (Color on line) Crystal structure (a) and Photoemission Electron Microscopy (PEEM) images of a  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  surface, taken at the Bi 5d (b) and Se 3d (c) core levels with 100 eV photons. Field of view in the PEEM images is  $20 \times 20 \mu\text{m}$ . Bright (dark) contours reflect regions of high (low) photoemission intensities.

Bruker APEX II diffractometer using Mo  $K\alpha$  radiation at room temperature. Unit cell determination and refinement, and data integration were performed with Bruker APEX2 software. The crystal structure was determined using SHELXL-97 implemented through WinGX.

The ARPES experiments were carried out on a Scienta SES-100 electron spectrometer at beamline 12.0.1 of the Advanced Light Source. The spectra were recorded at photon energies ranging from 35 to 100 eV, as indicated in the text, with a combined instrumental energy resolution of  $\sim 12$  meV and an angular resolution better than  $\pm 0.07^\circ$ . Samples were cleaved at low temperature (15-20 K) under ultra-high vacuum (UHV) conditions. The temperature was measured using a silicon sensor mounted near the sample. The SARPES experiments were performed at beamline U5UA at the National Synchrotron Light Source using a Scienta R4000 electron analyzer coupled to a pair of mini-Mott spin polarimeters that enable measurements of both the in-plane and out-of plane spin polarizations. The spin-resolved data were recorded at 58 eV photon energy, with the sample kept at  $\sim 300$  K. Energy and angle resolution were approximately 40 meV and  $0.5^\circ$ , respectively. Photoemission Electron Microscopy (PEEM) experiments were carried out at the XPEEM/LEEM end-station at the National Synchrotron Light Source beamline U5UA at room temperature, with 100 eV photons using an Elmitec SPE-LEEM III microscope. All the samples were cut from the same bulk piece and cleaved and measured in ultrahigh vacuum conditions (base pressure better than  $2 \times 10^{-9}$  Pa in the ARPES and SARPES chambers and better than  $2 \times 10^{-8}$  Pa in the PEEM chamber).

Electronic structure calculations were performed in the framework of density functional theory (DFT) us-

TABLE I: Structural Characterization of  $\text{Bi}_4\text{Se}_{2.56}\text{S}_{0.44}$ . Space group R3(No. 148),  $a = 4.2466(8) \text{ \AA}$ ,  $c = 39.706(7) \text{ \AA}$ , 329 unique reflections,  $R_1$  (all reflections) = 0.0457,  $wR_2 = 0.0938$ ,  $\text{GooF} = 1.109$ .

Atom	Wyck.	x	y	z	Occ.	$U_{11}$	$U_{33}$	$U_{12}$
Bi (1)	6c	0	0	0.14390(3)		0.0227(4)	0.0307(6)	0.0114(2)
Bi (2)	6c	2/3	1/3	0.04505(2)		0.0200(4)	0.0262(6)	0.0100(2)
Se (1)	6c	1/3	2/3	0.08384(8)		0.0276(9)	0.0340(17)	0.0138(4)
Se (2)	3a	0	0	0	0.56(2)	0.024(2)	0.024(3)	0.0122(10)
S (2)	3a	0	0	0	0.44(2)	0.024(2)	0.024(3)	0.0122(10)

ing the WIEN2K [23] code with a full-potential linearized augmented plane-wave and local orbitals [FP-LAPW + lo] basis [24–26] together with the PBE parameterization [27] of the GGA for the exchange-correlation functional. The plane wave cut-off parameter  $R_{MT}K_{MAX}$  was set to 7 and the irreducible Brillouin zone (BZ) was sampled by 288 k-points. Spin orbit coupling (SOC) was included. For  $\text{Bi}_4\text{Se}_3$  the reported crystal structure [28] was used. To estimate the effect of the partial S substitution for Se, electronic structure calculations were also performed for  $\text{Bi}_4\text{Se}_2\text{S}$ . For this material a fully ordered structure was taken (with S fully occupying the middle layer in the quintuple layer part of the structure) and the lattice constants were interpolated linearly, according to Vegard's law [29], using our data for the structure of  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$ .

Figure 1 shows a schematic view of the crystal structure of  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  and PEEM images of a cleaved surface. The details of the structural characterization are given in Table 1; the structure determination was used to precisely define the crystal composition. The two PEEM micrographs show the same spot on the surface recorded at two different kinetic energies of photo-electrons, corresponding to the Bi 5d and Se 3d core levels. The inversion of contrast between Bi 5d and Se 3d micrographs indicates that the surface consists of alternating  $\text{Bi}_2$  and Se terminated terraces. The terrace width is of the order of a few  $\mu\text{m}$ . As the photon spot sizes in our ARPES and SARPES experiments are around  $50 \mu\text{m}$  and  $0.5 \text{ mm}$ , respectively, the photoelectron characterization represents an average over the two types of terraces.

In Figure 2 we compare the experimentally determined electronic structures of  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  and  $\text{Bi}_2\text{Se}_3$ . The Bismuth core level (5d) spectra (Fig. 2(a)) clearly indicate two different chemical environments for Bi atoms in  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$ : one is similar to the environment in  $\text{Bi}_2\text{Se}_3$ , whereas the other indicates the more metallic character of the  $\text{Bi}_2$  layers. The wide-energy range valence band spectra, shown in Figure 2 (b) and (c) are generally similar for the two materials, with a nearly rigid-band down-shift of  $\sim 0.4$  eV of the  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  spectrum relative to  $\text{Bi}_2\text{Se}_3$  yielding a good general correspondence of the bands. The high intensity feature in the  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  spectrum that crosses the Fermi level is the central point of this study - this is the TSS, similar to the one observed in  $\text{Bi}_2\text{Se}_3$ , but also down-shifted, with the Dirac point around 0.54

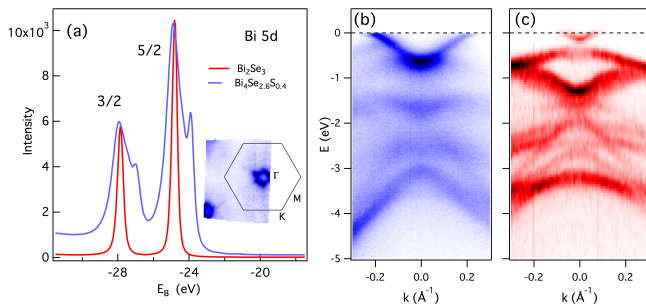


FIG. 2: (Color on line) Photoemission Spectra from  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  and  $\text{Bi}_2\text{Se}_3$ . (a) Bi 5d core-levels in  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  (blue) and  $\text{Bi}_2\text{Se}_3$  (red). Double peak structure of each spin-orbit split state indicates two chemically different bismuth sites in the  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  crystal. Inset shows the SBZ with the  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  Fermi surface measured with 59 eV photons. (b) Valence band along the  $\Gamma - M$  line in the SBZ for  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  and (c) for  $\text{Bi}_2\text{Se}_3$ .

eV below the Fermi level. This down-shift of both the valence bands and the TSS suggests that the major effect of the  $\text{Bi}_2$  layers in this natural superlattice phase is to donate electrons to the  $\text{Bi}_2\text{Se}_3$  quintuple layers. A wide  $k$ -space survey indicates that the TSS forms a hexagonally shaped Fermi surface at the center of the surface Brillouin zone (SBZ) (Fig. 2(a), inset). A new feature in the valence band spectrum in Fig. 2(b) is the “hole-like” state that crosses with the TSS at  $E \approx -0.15$  eV,  $k_x \approx \pm 0.15 \text{ \AA}^{-1}$ . This is a bulk state, as will be discussed further with reference to Fig. 3, which does not have an obvious counterpart in the  $\text{Bi}_2\text{Se}_3$  spectrum.

In Figure 3, we show the detailed spin- and  $k$ -resolved electronic structure of  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$ . Panels (a) and (b) show the photon energy dependence of the ARPES intensity at the Fermi level along the  $\Gamma - K$  line and at the center of the SBZ, respectively, for photon energies ranging from 50 to 84 eV in 2 eV steps. The intensity maps are converted into  $k$ -space by using the inner potential  $V = 10$  eV in the approximation for the out-of-plane momentum,  $k_z = \frac{1}{\hbar} \sqrt{2m(E_k \cos^2(\theta) + V)}$ , where  $E_k$  is the kinetic energy of a photoelectron. The straight features at  $k_y = \pm 0.173 \text{ \AA}^{-1}$  in Fig. 3(a) represent the Fermi surface of the TSS. The bulk hole state previously mentioned is visible here for negative  $k_y$  as a slightly dispersing (with  $k_z$ ) feature, intertwined around the TSS. The straight vertical line of high intensity in (b) corresponds to the Dirac point of the TSS. Slightly lower in energy, another bulk state can be seen as dispersing with  $k_z$ , with the minimum around  $k_z = 4.35 \text{ \AA}^{-1}$ . Both bulk features have the periodicity of  $\approx 0.5 \text{ \AA}^{-1}$ , suggesting that the relevant periodicity in real space in the  $z$  direction is  $\approx 12.5 \text{ \AA}$ . This is close to the thickness of one of the  $\text{Bi}_2$ - $\text{Bi}_2\text{Se}_3$  composite layers that repeats three times to form the rhombohedral unit cell (Fig. 1(a)). In panels

(c) and (f), we also show the in-plane ARPES intensity at the Fermi level for two photon energies,  $h\nu = 58$  and  $72$  eV, corresponding to  $k_z = 4.06$  and  $4.43 \text{ \AA}^{-1}$ , respectively. The hexagonally shaped contour represents the Fermi surface of the TSS. The dispersion of the surface state measured at  $h\nu = 58$  eV along two high symmetry directions in the SBZ is shown in panels (d) and (e). At  $h\nu = 72$  eV, the intensity at the Fermi level is strongly modulated by the nearly overlapping bulk state with the three-fold symmetry (Fig. 3(f)). The area enclosed by the TSS’ Fermi surface is almost an order of magnitude larger than that in pristine  $\text{Bi}_2\text{Se}_3$ , reflecting a surface electron concentration of  $\sim 8.7 \times 10^{12} \text{ cm}^{-2}$ . Such high surface electron doping can also be obtained on  $\text{Bi}_2\text{Se}_3$  through adsorption of various metals on its surface, producing a very similar hexagonal warping of the TSS’ Fermi surface [18].

Figure 3(g) shows the spin-resolved spectra with polarization defined in the  $y$  direction for points A and B from Fig. 3(c). The peak at the Fermi level, corresponding to the TSS, shows a significant spin polarization ( $\sim 30\%$ ) that reverses sign when the momentum is reversed ( $k_x \rightarrow -k_x$ ), an indication of the chiral spin structure. It is interesting to note that the chirality is opposite to that observed in  $\text{Bi}_2\text{Se}_3$  [8]. The peak at around  $-0.5$  eV also shows a polarization, but without the sign-reversal, an effect also observed in the bulk valence band in  $\text{Bi}_2\text{Se}_3$  [15]. The polarization of the TSS is much smaller in  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  than in  $\text{Bi}_2\text{Se}_3$  [8], probably due to the partial overlap with the bulk states.

Figure 4 shows a comparison of the calculated bulk band structures for  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_4\text{Se}_3$ ; SOC has a significant effect on the band structure of  $\text{Bi}_4\text{Se}_3$ . The lower red colored band in figure 4 (b), for example, has shifted by about 1 eV on the inclusion of SOC. The calculations predict  $\text{Bi}_4\text{Se}_3$  to be a semi metal with hole pockets at  $\Gamma$  and Z and an electron pocket at F. The hole pockets at  $\Gamma$  and Z project to the  $\bar{\Gamma}$  point in the SBZ and are seen in the ARPES measurement. The electron pocket predicted at the bulk F point is not observed by ARPES, suggesting that it lies higher in energy than is predicted by the calculations. Comparison of the band structures allows us to identify bands closely above and below  $E_F$  in  $\text{Bi}_4\text{Se}_3$  as being  $\text{Bi}_2\text{Se}_3$ -like bands that have been modified through interactions with the Bi bilayers; these are shown as red in the figure. Bands appearing directly around  $E_F$  (blue) in  $\text{Bi}_4\text{Se}_3$  are primarily  $\text{Bi}_2$  derived states modified by hybridization with the  $\text{Bi}_2\text{Se}_3$  layers.

There are two continuous gaps in the electronic structure for  $\text{Bi}_4\text{Se}_3$ , labeled as Gap 1 and Gap 2 in Figure 4. Counting all bands to Gap 1 gives, for the time-reversal-invariant momenta (TRIM) points of the bulk BZ [30], positive parity for  $\Gamma$ , Z, and L, and negative parity for F. Therefore in  $\text{Bi}_4\text{Se}_3$  we expect a TSS cone at the projection of the F point in the SBZ. According to the band structure calculation, the cone would be about 0.5 eV

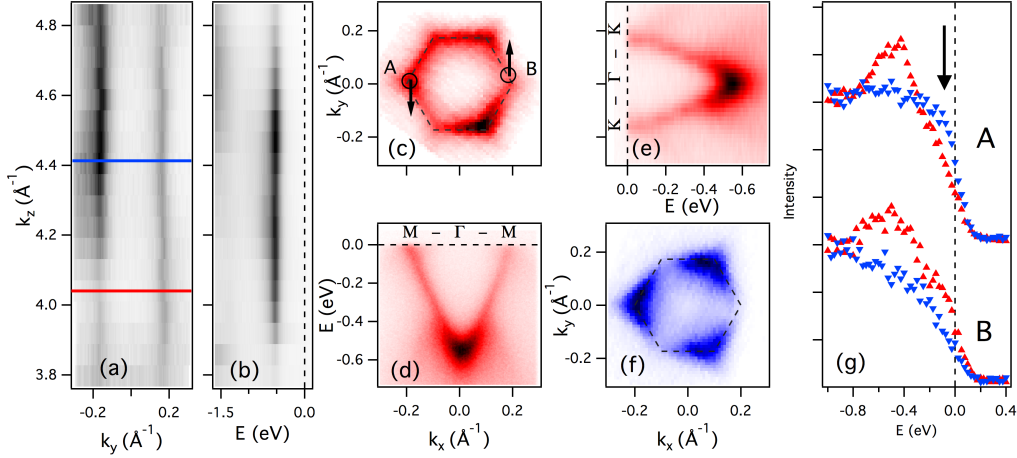


FIG. 3: (Color on line) Spin-resolved electronic structure of  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$ . (a) ARPES intensity at the Fermi level as a function of the in-plane ( $k_y$  along the  $\Gamma - K$  line) and out-of plane ( $k_z$ ) momentum. The two vertical lines of high intensity at  $k_y = \pm k_F \approx \pm 0.173 \text{ \AA}^{-1}$  correspond to the Fermi surface of the surface state from Fig. 2(b). (b) Intensity at the  $\Gamma$  point ( $k_x = k_y = 0$ ) of the SBZ as a function of  $k_z$ . The vertical line of high intensity at  $E = 0.54 \text{ eV}$  corresponds to the Dirac point of the surface state. (c) In-plane Fermi surface measured at  $k_z = 4.06 \text{ \AA}^{-1}$  and (f) at  $k_z = 4.43 \text{ \AA}^{-1}$ , corresponding to the red and blue lines in panel (a), respectively. The circles A and B in (c) indicate the  $k$ -positions where the spin-resolved measurements were performed, while arrows represent the in-plane spin polarization. Dispersion of the surface state along the  $\Gamma - M$  (d) and  $\Gamma - K$  (e) momentum lines in the SBZ, measured at  $k_z = 4.06 \text{ \AA}^{-1}$ . (g) SARPES spectra taken at A and B points in the SBZ, as indicated in (c). Red (blue) spectra represent spin-up (spin-down) components in the  $y$  direction. TSS is indicated by arrow.

below the Fermi energy (for  $\text{Bi}_4\text{Se}_2\text{S}$  we expect a second cone at the projection of the Z point, which also has negative parity, but since this would be above the Fermi level it would not be seen by ARPES). Counting the bands until Gap 2 yields, for both  $\text{Bi}_4\text{Se}_3$  and  $\text{Bi}_4\text{Se}_2\text{S}$ , TRIM points Z, M, and L with positive parity and  $\Gamma$  with negative parity. This would yield a TSS cone at  $0.5 \text{ eV}$  below the Fermi level at  $\Gamma$ . Note that counting to Gap 2 is equivalent to counting to the lower red band belonging to  $\text{Bi}_2\text{Se}_3$ ; we observe the same parity at each TRIM as is seen in pure  $\text{Bi}_2\text{Se}_3$ . When counting to Gap 1 one counts to a band belonging to the Bi bi-layer. The second cone at F might belong to the  $\text{Bi}_2$ , which was predicted to be a 2D quantum spin Hall system [21]. The crystal cleaves to expose  $\text{Bi}_2$  and  $\text{Bi}_2\text{Se}_3$  Se-terminated terraces, neither of which are at a bulk inversion center. In this case the projection of the bulk BZ points to the surface BZ is less certain, but since the only TRIM at the surface BZ are at  $\bar{\Gamma}$  and  $\bar{M}$ , the TSS must be at either of those two points. In ARPES we see one TSS cone at  $\bar{\Gamma}$  and no cone at  $\bar{M}$  (Fig. 2(a), inset). Where these surface states reside, i.e. on the  $\text{Bi}_2$  terraces, the  $\text{Bi}_2\text{Se}_3$  terraces, or both, and their relation to the bulk band structure, should be the subject of further study on this material.

$\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$  opens several interesting possibilities for studying the role of dimensionality in topological systems: as Fig. 3 shows, there is a 2D n-type TSS, nearly overlapping with a p-type bulk (3D) Fermi surface. In

addition, PEEM images from Fig.1 show alternating  $\text{Bi}_2$  - Se terminations, each kind of surface no doubt displaying a different surface electronic structure. Each step would then represent a boundary (or a junction) between two 2D (topological-'trivial' or topological-topological, n-n or p-n) electronic "gasses". This offers the possibility of studying topological phenomena ranging from 1D to 2D to 3D in a single system. The current ARPES experiments lack the necessary spatial resolution to observe such effects, but the scanning tunneling microscopy, for example, could provide information about these phenomena. A recent study of deposited Bi bi-layer on  $\text{Bi}_2\text{Te}_3$  [22] has indicated that similar phenomena might be at play in that system: with depositing bismuth, a hole-like state is added to the  $\text{Bi}_2\text{Te}_3$  bands. Although the authors consider the  $\text{Bi}_2$  layer to be homogeneous, it might be that terraces with mixed termination are formed in that case as well, creating a situation that is similar to what we observe in  $\text{Bi}_4\text{Se}_{2.6}\text{S}_{0.4}$ .

We acknowledge helpful discussions with B.A. Bernevig and C. Fang. The work at Brookhaven is supported by the US Department of Energy (DOE) under Contract No. DE-AC02-98CH10886. The work at Princeton University was supported by SPAWAR grant N66001-11-1-4110 and NSF DMR-0819860, and HWJ thanks ConocoPhillips for fellowship support. ALS is operated by the US DOE under Contract No. DE-AC03-76SF00098.



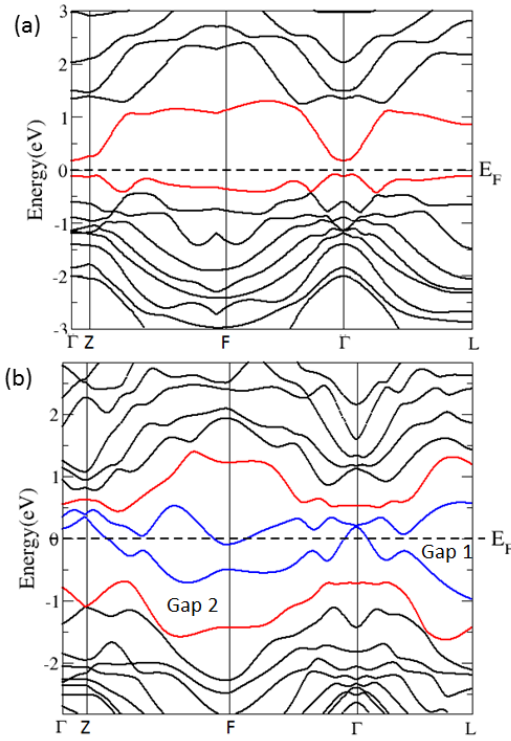


FIG. 4: (Color on line) Comparison of the bulk electronic band structures for (a)  $\text{Bi}_2\text{Se}_3$  and (b)  $\text{Bi}_4\text{Se}_3$ . Colored bands are described in the text.

\* Electronic address: valla@bnl.gov

† Electronic address: rcava@princeton.edu

- [1] L. Fu, C. L. Kane, and E. Mele, *Physical Review Letters* **98**, 106803 (2007), ISSN 0031-9007.
- [2] H.-J. Noh, H. Koh, S.-J. Oh, J.-H. Park, H.-D. Kim, J. D. Rameau, T. Valla, T. E. Kidd, P. D. Johnson, Y. Hu, et al., *EPL (Europhysics Letters)* **81**, 57006 (2008), ISSN 0295-5075.
- [3] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. S. Hor, R. J. Cava, and M. Z. Hasan, *Nature* **452**, 970 (2008).
- [4] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, *Nature Physics* **5**, 438 (2009), ISSN 1745-2473.
- [5] D. Hsieh, Y. Xia, L. Wray, D. Qian, A. Pal, J. H. Dil, J. Osterwalder, F. Meier, G. Bihlmayer, C. L. Kane, et al., *Science (New York, N.Y.)* **323**, 919 (2009).
- [6] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, et al., *Nature Phys.* **5**, 398 (2009).
- [7] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, et al., *Science* **325**, 178 (2009), ISSN 1095-9203.
- [8] Z.-H. Pan, E. Vescovo, A. Fedorov, D. Gardner, Y. Lee, S. Chu, G. Gu, and T. Valla, *Physical Review Letters* **106**, 257004 (2011), ISSN 0031-9007.
- [9] S. Xu, L. Wray, Y. Xia, R. Shankar, A. Petersen, A. Fedorov, H. Lin, A. Bansil, Y. Hor, D. Grauer, et al., *Arxiv preprint arXiv:1007.5111* (2010).
- [10] Z. Ren, A. A. Taskin, S. Sasaki, K. Segawa, and Y. Ando, *Phys. Rev. B* **82**, 241306 (2010).
- [11] H. Ji, J. Allred, M. Fuccillo, M. Charles, M. Neupane, L. Wray, M. Hasan, and R. Cava, *Physical Review B* **85**, 201103 (2012).
- [12] K. Nakayama, K. Eto, Y. Tanaka, T. Sato, S. Souma, T. Takahashi, K. Segawa, and Y. Ando, *Arxiv preprint arXiv:1206.7043* (2012).
- [13] T. Sato, K. Segawa, H. Guo, K. Sugawara, S. Souma, T. Takahashi, and Y. Ando, *Physical review letters* **105**, 136802 (2010).
- [14] Y. L. Chen, Z. K. Liu, J. G. Analytis, J.-H. Chu, H. J. Zhang, B. H. Yan, S.-K. Mo, R. G. Moore, D. H. Lu, I. R. Fisher, et al., *Phys. Rev. Lett.* **105**, 266401 (2010).
- [15] C. Jozwiak, Y. Chen, A. Fedorov, J. Analytis, C. Rotundu, A. Schmid, J. Denlinger, Y.-D. Chuang, D.-H. Lee, I. Fisher, et al., *Physical Review B* **84**, 165113 (2011), ISSN 1098-0121.
- [16] M. Bianchi, R. Hatch, J. Mi, B. Iversen, and P. Hofmann, *Physical Review Letters* **107**, 086802 (2011).
- [17] H. Benia, C. Lin, K. Kern, and C. Ast, *Physical Review Letters* **107**, 177602 (2011).
- [18] T. Valla, Z.-H. Pan, D. Gardner, Y. Lee, and S. Chu, *Physical Review Letters* **108**, 117601 (2012), ISSN 0031-9007.
- [19] Z.-H. Pan, A. Fedorov, D. Gardner, Y. Lee, S. Chu, and T. Valla, *Physical Review Letters* **108**, 187001 (2012), ISSN 0031-9007.
- [20] H. Lind and S. Lidin, *Solid state sciences* **5**, 47 (2003).
- [21] S. Murakami, *Physical Review Letters* **97**, 236805 (2006), ISSN 0031-9007.
- [22] T. Hirahara, G. Bihlmayer, Y. Sakamoto, M. Yamada, H. Miyazaki, S.-i. Kimura, S. Blügel, and S. Hasegawa, *Physical Review Letters* **107**, 166801 (2011), ISSN 0031-9007.
- [23] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave+ Local Orbitals Program for calculating Crystal Properties*, Technische Universität Wien, Austria (2001).
- [24] D. J. Singh and L. Nordström, *Planewaves, Pseudopotentials, and the LAPW Method*, Springer, New York, 2nd ed. (2006).
- [25] G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, *Phys. Rev. B* **64**, 195134 (2001).
- [26] E. Sjöstedt, L. Nordström, and D. J. Singh, *Solid State Communications* **114**, 15 (2000), ISSN 0038-1098.
- [27] J. P. Perdew, K. Burke, and M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
- [28] M. M. Stasova, *Izvestiya Akademii Nauk SSSR* **4**, 28 (1968).
- [29] L. Vegard, *Zeitschrift für Physik A: Hadrons and Nuclei* **5**, 17 (1921).
- [30] L. Fu and C. L. Kane, *Physical Review B* **76**, 045302 (2007).